φ and $\langle \omega^2 \rangle$ values obtained for the three crystal modifications at the various temperatures. The curve for W1 represents the average over the two independent molecules. The quantity $\langle \omega^2 \rangle^{1/2}$ corresponds to the half-width of a parabolic energy well at the height RT/2 above its minimum.¹⁶ The relative displacements of the three curves along the energy coordinate depend on the temperature, Y1 being the most stable at room temperature and W1 the most stable above about 375 K, as shown in Figure 2. The Y1 and LY1 curves are drawn at the same height since the phase transitions from Y1 to LY1 and from LY1 to Y1 have both been observed at about 375 K. The dashed curves connect the experimental energy wells and may be taken to portray in an approximate way the energy dependence on φ at a defect in the crystal and in a still more approximate way the energy profiles for the phase transformation.¹⁷ At the temperature corresponding to the transformation of Y1 to W1 (380-410 K)⁵ the extrapolated value for $\langle \omega^2 \rangle^{1/2}$ is quite sufficient to carry it across the barrier to LY1, which would then be an intermediate on the way to W1. This would agree with an earlier suggestion⁶ that some intermediate structure might be present in the initial stages of the phase transition, before nucleation of W1 sets in.

Further studies including high-temperature single-crystal NMR work are in progress on this interesting system.

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(17) The reaction paths are certainly more complicated than suggested by Figure 2, but the φ coordinate must represent an important component.

Kinetics of Iron(III) Porphyrin Catalyzed Epoxidations

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The discovery of model iron(III) porphyrin catalyzed oxidations which mimic the enzymatic epoxidation and hydroxylation reactions catalyzed by cytochrome P-450 has stimulated much interest in the kinetics and mechanisms of these model reactions.¹⁻⁶ These studies require stable catalysts, absence of interfering byproducts, and oxidants that are soluble and highly reactive toward the catalyst but not toward the alkene. Although iron(III) tetraphenylporphyrin is rapidly destroyed during catalytic epoxidation by peracids or iodosylbenzenes,⁶ the introduction of bulky and electronegative substituents on the phenyl rings has been shown to greatly reduce this catalyst destruction.^{7,8} Peracids are not sufficiently reactive with iron(III) porphyrins and they react directly with alkenes.⁸⁻¹⁰ Iodosylbenzene is much more reactive

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Figure 1. Spectra of reactants and product solutions in CH₂Cl₂/ CH_3OH/H_2O (80:18:2). (···) Computer sum of a solution 8.9 × 10⁻⁶ M TDCPPFeCl and a solution of 0.5 M norbornene and 10^{-3} M F₅C₆IO. -) Spectrum of a solution originally having these concentrations after a kinetic run. (--) Spectrum of the same solution after addition of a second aliquot of the F_5C_6IO to make the solution again 10^{-3} M in this oxidant. The spectrum was taken after the second kinetic run. Solvent base line was subtracted from all spectra.



Figure 2. Plots of $A - A_{\infty}$ and $\ln (A - A_{\infty})$ vs. time for a solution of 4.2 \times 10⁻⁶ M TDCPPFeCl, 1.0 M norbornene, and 10⁻³ M F₅C₆IO in CH₂Cl₂/CH₃OH/H₂O (80:18:2) at 25 °C. Only one of every 20 points is plotted. Rate data are calculated using all points.

toward the catalysts than toward alkenes.⁸ However, iodosylbenzenes are insoluble in methlene chloride, ketones, etc.

We wish to report oxidant systems that meet all the criteria for kinetic studies of very rapid, high turnover catalyzed epoxidation without catalyst destruction, along with preliminary kinetic results with these systems.

Pentafluoroiodosylbenzene (PFIB)^{8,11} reacts directly with only the most strained or electron-rich alkenes but reacts very rapidly with iron(III) porphyrins even in methylene chloride where it is insoluble. However, it dissolves readily in alcohols where its reactivity is reduced. Addition of water and methylene chloride increases the reaction rate. Systems we have found convenient for rapid oxidations are methylene chloride/trifluoroethanol/water (80:18:2) or methylene chloride/methanol/water (80:18:2). Concentrations of PFIB up to 0.03 M are obtainable.

In these solvent systems PFIB reacts very slowly, if at all, with alkenes but very rapidly with the catalysts as shown below.¹²

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⁽¹²⁾ In either this or the methanol solvent system, iron(III) tetraphenylporphyrin and iron(III) tetramesitylporphyrin are destroyed during the kinetic runs.

Table I. Kinetics of Iron(III) Porphyrin Catalyzed Epoxidations at 25 °C

catalyst R	catalyst concn, M	solvent (ratio by volume)	oxidant ^a concn, M	alkene ^b concn, M	wavelength	$k_{\rm obsd}$, s ⁻¹	$k_1 \times 10^{-3}, M^{-1} s^{-1}$
CF, d	4×10^{-6}	B, 80:18:2 ^e	1×10^{-3}	0.5 N	280	0.002	0.5
3-0-3	2×10^{-5}	A, 45:45:10	4×10^{-3}	0.15 Cy	290	1.4	70
CI.d	5×10^{-7}	A, 89:10:1 ^e	1×10^{-3}	0.01 C	280	0.025	50
	5×10^{-7}	A. 89:10:1	1×10^{-3}	0.5 Cy	280	0.025	50
$\gamma $	5×10^{-7}	A, 89:10:1	1×10^{-3}	0.5 H	280	0.022	44
\preceq	7×10^{-7}	A, 89:10:1	1×10^{-3}	0.5 N	280	0.02	30
cı	5×10^{-7}	A, 78:20:2	1×10^{-3}	0.5 N	280	0.13^{f}	26
	4.2×10^{-6}	B. 80:18:2	0.03	0.5 N	350	0.004	1.0 ^g
	4.2×10^{-6}	B . 80:18:2	1×10^{-3}	1.0 N	285	0.008	1.9
	4.2×10^{-6}	B. 80:18:2	1×10^{-3}	0.5 N	285	0.008	1.8
	7.1×10^{-6}	B, 80:18:2	1×10^{-3}	0.2 N, 0.2 C	285	0.012	1.7
	4.2×10^{-6}	B, 80:18:2	1×10^{-3}	0.25 N	285	0.006	1.4
	4.2×10^{-6}	B . 80:18:2	1×10^{-3}	0.01 N	285	0.005	1.28
	4.2×10^{-6}	B , 80:18:2 ^h	1×10^{-3}	0.5 H	285	0.003	0.8
	9×10^{-6}	B. 80:18:2 ^h	1×10^{-3}	0.5 Cy	285	0.018	2.2
	9×10^{-6}	B, 80:18:2 ^h	1×10^{-3}	0.5 V	285	0.018	1.9
	5×10^{-6}	B , 80:18:2	10 ⁻³ PhIO	0.5N	285	0.005	1.0

^a The oxidant is pentafluoroiodosylbenzene unless specified otherwise. ^bAlkene abbrevations: N = norbornene, C = cis-cyclooctene, Cy = cyclohexene, H = cis-2-hexene, V = vinyltrimethylsilane. ${}^ck_1 = k/[catalyst]$. ^dHemin syntheses are described elsewhere.[§] ^e The solvent A is CH₂Cl₂/CF₃CH₂OH/H₂O, and B is CH₂Cl₂/CH₃OH/H₂O. ^fThe first-order rate plot was somewhat curved. ^gThe Soret band shifted to lower wavelength in these runs indicating some methanol oxidation to formic acid. ^hThese solutions contained 0.1 M formic acid which removed an inhibition period. Norbornene oxidation is unaffected by this concentration of formic acid.

Furthermore, as in the heterogeneous reactions,⁸ yields of epoxides are nearly quantitative and turnovers high (e.g., $10\,000$ epoxides/catalyst). We interpret this reaction in alcohols as an addition to the iodosylbenzene to produce a "peracid-like" compound (I), in analogy to the conversion of iodosylbenzene to

$$R-I-O + HOR' \xrightarrow{K_1} R-I(OH)OR' \xrightarrow{K_2} R-I(OR')_2$$
(1 and 2)

dimethoxyiodobenzene reported by Schardt and Hill.3b

Fortunately, as depicted in Figure 1, the absorptions of iodosylbenzenes in alcohols from 250 to 350 nm greatly exceed those of either the iodobenzenes or the iron(III) porphyrins, providing a very convenient method of following the kinetics, some of which require stopped-flow techniques.

Figure 2 shows plots of absorbance vs. time and log $(A - A_{\infty})$ vs. time at 285 nm after the addition of 4.2×10^{-6} M iron(III) tetrakis(2,6-dichlorophenyl)porphyrin chloride to a solution of 0.001 M PFIB and 1.0 M norbornene in methylene chloride/ methanol/water (80:18:2). The final spectrum and GLC analyses indicated complete conversion to the iodobenzene and the epoxides. Similar results were obtained with iodosylbenzene although the rates of reaction are slower. Table I summarizes kinetic data with several alkenes, solvent systems, etc.

The first-order rate constant varies with solvent composition. In 80% methylene chloride/20% trifluoroethanol the reaction is accelerated by the addition of water up to about 2% water in the solvent. This is consistent with the postulated equilibria of eq 1 and 2 and suggests that the dihydroxy derivative is not formed since iodosylbenzenes are insoluble in water. The reaction rate is about the same in 89:10:1 methylene chloride/trifluoroethanol/water as in a 78:20:2 mixture of the same components. However, substitution of methanol for trifluoroethanol reduces the rate constant by a factor of 10.

This reaction is very fast (e.g., $t_{1/2} = 25$ s at 5×10^{-7} M catalyst) and can occur with high (~10⁴) turnover without catalyst destruction. Turnover rates as high as 300 (epoxides/catalyst)/s for norbornene epoxidation are easily obtained. The reaction is first order in oxidant for both iodosylbenzene and pentafluoro-iodosylbenzene over the wide concentration range used (from 10⁻⁴)

to 3×10^{-2} M). It is also first order in the catalyst and essentially independent of concentration or structure of the alkene.¹³ The second-order rate constants thus obtained are 6×10^4 M⁻¹ s⁻¹ in the trifluoroethanol solvent and 2×10^3 M⁻¹ s⁻¹ in the methanol solvent using pentafluoroiodosylbenzene and iron(III) tetrakis-(2,6-dichlorophenyl)porphyrin.¹⁴ The kinetics of these reactions under our conditions are described in eq 1.

$$\frac{d(epoxide)}{dt} = \frac{-d(RIO)}{dt} = k_1(Hm^+)(RIO)$$
(3)

Although solvent effects and prelminary studies of general-acid catalysis suggest a more complex form of eq 3, it is not yet possible to express the rate as a function of other concentrations.

It is interesting that the rates of reaction of pentafluoroiodosylbenzene and iodosylbenzene differ by less than a factor of 2 in solution in contrast to the two-phase reactions in methylene chloride where the former reacts much faster than does iodosylbenzene.⁸ These results and the solvent effect of rate suggest that the driving force is in the stability of the $R'O^-$ leaving group rather than the iodobenzene.



ROH + BH+ (4)

As in the case of hemin-catalyzed phenol oxidation,⁹ these kinetics do not provide evidence concerning the mechanism of

⁽¹³⁾ In the absence of substrate, methanol is oxidized more slowly than are alkenes even though hemin is not destroyed. Thus, high-valent iron intermediates do seem to accumulate and alkene dependence should appear under some conditions.

⁽¹⁴⁾ These rapid rates can be contrasted to a bimolecular rate constant for the reaction of iron(III) tetraphenylporphyrin and iodosylbenzene in pure ethanol of about 1 M^{-1} s⁻¹ reported by Shannon and Bruice.^{4b} Clearly, water has a large effect on the rate.

oxygen transfer to the alkene except to show that intermediates are extremely unstable, making reaction 5 much faster than reaction 4.

$$-Fe^{+} + C = C \left(\frac{k_2}{fost} \right) C + -Fe^{+} (5)$$

The discovery of a homogeneous, rapid, and high-turnover catalytic epoxidation system, whose kinetics are easily followed, provides a means of determining detailed mechanisms of this reaction as well as that of catalyzed hydroxylation.¹³ The nature of the iodosylbenzene species in solution and the nature of their reactions with metalloporphyrins are under study.

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Oxidation of Phosphazine by Singlet Oxygen. High-Field ³¹P NMR Spectroscopic Studies of 3-Phospha-1,2-dioxa-4,5-diazine and Phospha-1,2-dioxetane

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Extensive studies have been focused on the reaction of singlet oxygen with conjugated dienes, and the simplest view of this reaction as a concerted [2 + 4] cycloaddition is widely accepted.¹⁻³ Meanwhile, only little attention has been drawn to photooxygenation of azines (1a),4-8 nitrogen analogues of acyclic conjugated dienes, and phosphazines (1b)⁹ in connection with chemiluminescent systems.¹⁰ Lechtken reported the formation of acetone from the direct decomposition of 1,2-dioxa-4,5-diazine (2a) formed by the photooxygenation of acetone azine and observed the chemiluminescence of the products.⁵ Suzuki et al. also described a similar type of photooxygenation of benzophenone and fluorenone triphenylphosphazine, which forms 3-phospha-1,2-dioxa-4,5-diazine (2b) and phospha-1,2-dioxetane (3b) as intermediates, and the chemiluminescence of the products.⁹



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Meanwhile, Landis proposed a free-radical pathway initiated by singlet oxygen to give a linear peroxide polymer.⁷ No direct evidence for the formation of 1,2-dioxa-4,5-diazine 2, however, was revealed at all. We wish to present here the first direct observation of 3-phospha-1,2-dioxa-4,5-diazine (2b) and its thermal decomposition product, phospha-1,2-dioxetane (3b) by high-field ³¹P NMR spectroscopy.¹¹

Photooxygenation of 1,1,3,3-tetramethyl-2-indanone triphenylphosphazine $(1c)^{12}$ at 15 °C afforded the corresponding ketone and triphenylphosphine oxide as major products accompanied with a small amount of 2,2,5,5-tetramethyl-3,4-benzo-3penten-5-olide. A strong light emission was also observed when the reaction was carried out at -78 °C and then warmed to room temperature.¹³ These findings encouraged us to carry out an exploratory experiment to observe the suspected intermediates.

A tetrahydrofuran solution (2 mL) of phosphazine 1c (1.4 \times 10^{-1} M) with polymer-bound rose bengal¹⁴ as a sensitizer was irradiated at -100 °C for 3 h with bubbling oxygen with two 500-W halogen lamps. A characteristic feature of the suspected intermediate, diazine 2c, is seen in the ³¹P NMR spectrum (-100 °C). Two resolved singlets appeared at -44.3 and -47.1 ppm in a ratio of 1:1, respectively, together with two other singlets at 25.8 (triphenylphosphine oxide) and 15.1 ppm (unreacted 1c). The



course of the decomposition of 2c was monitored with temperature. No change was observed in the spectrum between -100 and -90 °C. When the sample was warmed to -80 °C, the diazine peaks decreased and a new singlet arose at -53.4 ppm presumably due to the formation of dioxetane 3c. At -70 °C, the diazine peaks completely disappeared and the dioxetane peak still remained. Finally, all transient peaks in the spectrum disappeared at 27 °C.

Two important results are evident for these experiments. That the ³¹P NMR spectrum revealed pairs of singlets between -44 and -48 ppm might be best explained by intramolecular ligand reorganization; i.e., pseudorotation between two conformers (2c' and 2c'') of diazine 2c.^{15–17} Pseudorotation using the azo group as pivot may easily take place. At low temperature, however, the pseudorotation process becomes slow and the separate signals might represent 2c' and 2c''.¹⁸ Diazine 2c undergoes thermal

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(18) 2c decomposed before coalescence temperature. An approximate value of k_c , the rate constant at coalescence, may be calculated from the expression, $k_c = \pi 2\nu/2^{1/2}$, where 2ν is the maximum chemical shift difference (in hertz) between the separate signals; hence, in this case, $k_c = \pi \times 464/2^{1/2}$ = 1 × 10³ s⁻¹.^{16b}

⁽¹¹⁾ High-field ³¹P NMR spectra were recorded by a JMN(JEOL) JX-400 NMR spectrometer at 161.8 MHz (broad-band proton decoupling) in 10 mm diameter NMR tube in tetrahydrofuran using phosphoric acid as an internal standard.